



(51) International Patent Classification 6:	Г	(11) International Publication Number: WO 97/4484
H01M 4/62	A1	(11) International Publication Number: YV 97/4464
11011/1 4/02	A1	(43) International Publication Date: 27 November 1997 (27.11.97
(21) International Application Number: PCT/US (22) International Filing Date: 13 May 1997 (		(AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU
<ul> <li>70) Priority Data:         <ul> <li>08/653,145</li> <li>24 May 1996 (24.05.96)</li> </ul> </li> <li>71) Applicant: W.R. GRACE &amp; COCONN. [US/UK Avenue of the Americas, New York, NY 10036 (I.</li> <li>72) Inventors: BLOCK, Jacob; 14112 Parkvale Road, R</li> </ul>	JS). ockville	Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
MD 20833 (US). FAN, Xlyun; 2907 Bear Trails, TX 77632 (US). 74) Agent: TROFFKIN, Howard, J.; W.R. Grace & Cc 7500 Grace Drive, Columbia, MD 21044 (US).		
		:
4) Title: IMPROVED ELECTRODE COMPOSITIONS		
7) Abstract		
An electrode composition for use as an electrode in a retive powder in a solid polymer and, as a dispersant, a polectrochemically inert at 2.5-4.5 volts.	non-aqu lyester j	ous battery system. The electrode composition contains an electrically olyamine copolymer that is electrochemically inert. The dispersant is

# FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL.	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuanis	SK	Slovakia
AT	Austria	FR	Peance	LU	Luxembourg	SN	Senega)
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
SA	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MC	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	мк	The former Yugoslav	TM	Tuckmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	BU	Honesov	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	treland	MN	Mongolía	UA	Ukraine
BR	Brazil	IL.	Israel	MK	Mauritania	υG	Uganda
BY	Belarus	IS	Iceland	· MW	Malawi	US	United States of Americ
ČA.	Canada	IT	Italy	МX	Mexico	uz	Uzbekistan
CF	Central African Republic	.IP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrxyzstan	NO	Norway	zw	Zimbabwe
CI	Citie d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon	•••	Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Rosnania		
cz	Czech Republic	ič	Saint Lucia	RU	Russian Federation		
DE:	Germany	ũ	Liechtenstein	SD	Sudan		
DK.	Denmark	ī.K	Sri Lanka	SE	Sweden		
EE.	Estonia	LR	Liberia	SG	Singapore		

WO 97/44841 PCT/US97/08032

## IMPROVED ELECTRODE COMPOSITIONS

This invention was made with Government support under contract DE-FC02-91CE 50336 awarded by the United States Department of Energy. The Government has certain rights in this invention.

## Background of the Invention

10 Field of the <u>Invention</u>:

This invention pertains to battery components, including electrodes, and cells.

## Description of the Related Art:

Storage batteries have a configuration composed of at least one pair of electrodes of opposite polarity and, generally, a series of adjacent electrodes of alternating polarity. The current flow between electrodes is maintained by an electrolyte composition capable of carrying ions across electrode pairs.

Non-aqueous batteries have certain distinct advantages over other types of storage batteries. They use, as anodes, light weight metals, such as alkali metals as for example, lithium metal, lithium oxides, lithium-aluminum alloys and the like which are at the far end of the electromotive series. These batteries have the potential for providing much higher specific energy (gravimetric) and volumetric energy densities (capacity per unit weight and volume, respectively) than other types of batteries, due to the low atomic weight of the metal and high potential

30

5

15

20

for forming a battery in conjunction with suitable positive electrodes far removed from the light weight metal electrode (the description herein will use batteries having lithium as the light weight metal anode although other light weight metals can be used) in the electromotive series. The battery can be formed in any conventional physical design, such cylindrical, rectangular or disc-shaped "button" cells, normally of a closed cell configuration.

10

15

The battery components of positive electrode, negative electrode and an electrical insulating material capable of permitting ionic conductivity, such as porous separator membranes or a solid or gel polymer electrolyte located between the electrodes. Batteries formed of these components can be in the form of distinct alternating plates in a sandwich design or of a continuously spirally wound design as are well known.

20

As disclosed in copending U.S. patent applications, U.S. Serial No.\_\_\_\_\_\_\_\_(Attorney Docket No. 8788), U.S. Serial No.\_\_\_\_\_\_\_(Attorney Docket No. 8878), U.S. Serial No.\_\_\_\_\_\_\_(Attorney Docket No. 9189), and U.S.

25

Serial No. \_\_\_\_\_\_\_(Attorney Docket No. 9190), co-assigned with the present application which teachings are incorporated herein by reference, methods and battery compositions have been developed which provide a solid polymer electrolyte-electrode composite suitable for light weight metal battery systems.

30

Briefly, the processes involve forming electrodes composed of active solid material which are co-

10

15

20

25

3.0

extruded with solid polymer electrolyte components to provide the resultant electrode-electrolyte composite. Solid material suitable for forming anodes include, for example, carbons capable of intercalating the light weight metal ions within its crystal or other structure, such as graphite or coke and the like, Solid material suitable for forming cathodes are metal chalcogenides having a metal selected from Ti, Zr, Nb, Cu, Fe, Ta, V, Mn, C, Co, Ni and mixtures of these metals alone or together with intercalating metals, such as lithium or sodium. Preferred alkali metal (e.g. lithium) chalcogenides are those of manganese oxides, cobalt oxides, vanadium oxide or nickel oxides or mixtures thereof. The most preferred chalcogenides are lithium manganese dioxide and overlithiated manganese oxides. The electrochemically active material is normally used in combination with minor amounts of up to about 30 wt. % of a conductive carbon based on the total solids. The conductive carbon may be a carbon black, such as acetylene black and usually has a particle size range of from about 1 to 100 mm. According to the embodiments disclosed, the solid polymer electrolyte is a blend of an electrolyte salt, a binder, and an organic liquid capable of solvating and forming an ionic complex with the salt. The salt is preferably a lithium salt selected from the group consisting of LiPF, LiAsF, LiCF,SO, and LiClO, and the like.

The liquids useful in forming the solid polymer electrolyte include the aprotic organic solvents, i.e., not prone to contributing a proton, such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, dimethyl adipate, tetramethylene sulfone, g-butyrolactone, dimethylformamide, dioctyl phthalate, and dibutyl phthalate and the like and mixtures thereof.

Polymers typically used in SPE's include polyacrylonitrile (PAN), poly(tetraethylene glycol diacrylate) (PEGDA), poly(vinylidene difluoride) (PVDF) and poly(vinyl pyrrolidinone) (PVP) and the like.

The various processes can be used to formulate composite electrolyte-anodes or electrolyte-cathodes, depending on the active electrode material utilized. The compounded composition typically is extruded into a desired shape, such as a sheet, which may be deposited onto a conductive current collector (foil, screen of metal) that can be cut into smaller sizes to form electrodes. The electrodes can then be assembled into batteries.

It is highly desirable to have a formulation that results in a final product having the desired characteristics, and one that is easily handled during processing. In extrusion processes, viscosity of the material is an important concern. The viscosity should be high enough to permit good mixing of the components to provide a homogeneous mass, while not being of such high viscosity to cause excessive back pressure in the extruder. At the same time the final product must have a high content of solid active particulate material to provide a suitable electrode.

The formulations and extrusion processes optionally utilize additives to modify various properties of the materials during fabrication, such

3.0

25

10

15

20

3NSDOCID: <WO\_\_\_\_\_9744841A1\_/\_>

10

15

20

25

30

as viscosity, and to enhance the characteristics of the final product. Typical of the additives used are dispersants. It might be assumed that a wide variety of dispersants might be useful to obtain the desired results. However, it has been found that, although there is a large number of dispersants available, most dispersants do not aid in enhancing the processing characteristics of the complex mixture of solid particulate material and solid polymer electrolyte (SPE) components. The SPE materials are generally fluid, low viscosity compositions under extrusion processing conditions. In addition, a selection of a particular dispersant is not obvious to the artisan when attempting to provide an extruded, highly-filled electrode, due to the many factors that influence the results one obtains with any particular dispersant. Among the factors that influence the results obtained are: (1) the solubility of the dispersant in the polymer electrode systems and/or organic electrolytes that are required in the application; (2) the chemical stability of the dispersant at the electrode potential realizing that many cells are operated at different potentials; (3) the stability of the electrochemically active and electrically conductive materials used in combination with a particular dispersant and under the conditions needed for fabrication; (4) the ability of the dispersant to allow or enhance binding of the active materials and other particulate material into a unitary structure at very low concentrations in order to provide an electrode with good performance; (5) the ability and ease of obtaining a uniform distribution of the dispersant with the binder and active material

1.0

1.5

20

25

30

ENSDOCID: «WO\_\_\_\_\_\_9744841A1\_I\_>

of the electrode; (6) the ability of the dispersant to remain stable in an electrode capable of undergoing a multiplicity of charge-discharge cyclings; (7) the number and ease of the steps required to obtain the desired electrode; and (8) the safety, availability of the material, and cost.

# Summary of the Invention

The present invention is directed to the addition of polyester/polyamine dispersants that are non-active and electrochemically stable (inert electrochemically) which produces a significant viscosity reduction to a feed mixture which has a high content of solid particulate active electrode material while providing an electrolyte-electrode composite product. This enables the obtainment of higher loadings of electrically active powder in the electrode, e.g. LiMn,O, in the cathode, or carbon in the anode. Preferably, the polyester/amine dispersant is electrochemically stable at 2.5 to 4.5 volts, most preferably 2.5-4.2 volts, as determined by standard procedures.

# Detailed Description of the Invention:

The present invention is directed to an improved extrusion process to provide high energy electrode-electrolyte composite products. The present process has been found to achieve higher loading of solid active electrode product in which the dispersant is an electrochemically inert material; and which achieves

10

15

20

25

30

good flow-through processing properties within the

The electrode compositions to which the present invention has been found suitable are those described in co-pending application Serial

No.\_\_\_\_\_\_\_\_\_\_(Attorney Docket No. 8788), U.S.

Serial No.\_\_\_\_\_\_\_\_\_\_(Attorney Docket No. 8878), U.S.

Serial No.\_\_\_\_\_\_\_\_\_\_(Attorney Docket No. 8878), U.S.

Serial No.\_\_\_\_\_\_\_\_\_\_\_(Attorney Docket No. 9189), and U.S. Serial No.\_\_\_\_\_\_\_\_\_\_(Attorney Docket No. 9190), which teachings are incorporated herein by reference. The present invention can be used most preferably in the process of the above application having Docket Nos. 9190, 8788, and 9189.

It has been unexpectedly found that the addition of certain dispersants which are classified as polyester/polyamine dispersants; - that is having

of certain dispersants which are classified as polyester/polyamine dispersants; - that is having ester and amine hydrophilic groups, provide a significant viscosity reduction during the extrusion processing of the materials; permit very high loading of solid active material; and provide an electrode in which the dispersant is an inert material therein. The polyester/polyamine dispersant must exhibit electrochemical stability (inertness) at an operating range of from 2.5 to 4.5 volts, most preferably from 2.5 to 4.2 volts, as determined by standard battery operating procedures.

Hypermer® KD1, available from ICI Americas, Inc. has been used to particular benefit. Hypermer® KD1 polyester/polyamine, when used as a dispersant in forming polymer electrode compositions, both anode and cathode, produces a significant viscosity reduction without deteriorating the electrochemical performance.

This unexpectedly enables the obtainment of higher loadings of electrically active powder in the cathode or in the anode, e.g., LiMn,0, in a cathode, or carbon in an anode.

The dispersant can be premixed with one or more of the components used in forming the desired composite electrolyte-electrode. Normally the dispersant is added as part of the initial feed mixture where more than one feed stream is used. The dispersant is preferably added to the solid active material. The dispersant should be used in from about 1 to about 3 percent of the total composition.

The preferred polymeric dispersant, is Hypermer® KD1. Other Hypermer dispersants having different solubility and stability characteristics have not been found suitable in achieving the desired result. For example, a series of these dispersants are known to have the following characteristics:

- (1) HYPERMER® KD1 for use in medium polarity solvents, e.g., ethers, ketones, THF, chlorinated hydrocarbons, and blends of these solvents.
- (2) HYPERMER® KD2 for use in highly polar solvents, e.g., ethanol, iso-propanol, 2-ethyoxy ethanol and some aqueous systems.
- (3) HYPERMER® KD3 and HYPERMER® KD4 for use in non-polar systems, e.g., mineral spirits, toluene, xylene, paraffin waxes and oils. Additional characteristics of certain hypermer products are shown in the following Table A:

30

25

5

10

15

- 9 -

TABLE A
Physical Characteristics

HYPERMER® Polymeric Dispersant	Appearance	Melting Point °C'	Specific Gravity	Viscosity (cps)	Effective Solvent Polarity Range
KD1	Tan colored flakes	Softens 60°C	1.05	N/A	Medium Polar
KD2	Straw colored liquid	N/A	1.02	200-320 at 20°C	Highly Polar
KD3	Amber liquid/ paste	Pourable 25°C	0.92	1600-2200 at 35°C	Non-polar

5

## Example 1

10

15

This example shows how the viscosity of a solid polymer electrolyte (SPE) mixture (without the electrically active component) is determined.

A solid polymer electrolyte composition according to the present invention was prepared, as follows:

#### Solid Polymer Electrolyte (SPE)

- wt. % Component
- 20 44 Ethylene Carbonate (Aldrich)
  - 44 Propylene Carbonate (Grant Chemicals)
  - 6 Polyacrylonitrile (Eastern Chemical)
  - 5 Lithium (bis) trifluoromethanesulfonimide (3M)
- 25 The mix was heated to 120°C while mixing to form a uniform mixture.

The viscosity of the mixture was determined as follows:

 $\lambda$  Brookfield RVT-DV-II viscometer was used with a "Thermosel" attachment. The temperature was 125°C. A number 27 spindle was used. The viscosity of this mixture was found to be 150 cp at shear rates between 6.8-34 sec $^{1}$ .

## Example 2

10

15

20

5

This example compares the viscosity of the basic SPE mixture of Example 1 with the same mixture containing an electrically active component (LiMn,O.), such as would be used to form an electrolyte-electrode composite according to the present invention.

LiMn,0, powder (obtained from the Davison Chemical Division of W.R. Grace) (20.17 parts per 10 parts SPE) was added to the mixture of Example 1, and the viscosity was determined as in Example 1. The viscosity was found to have increased to 12,500 cp at 6.8 sec<sup>-1</sup>. At 3.4 sec<sup>-1</sup>, the viscosity was 16,400 cp, and at 0.85 sec<sup>-1</sup>, the viscosity was 76,800 cp.

## Example 3

25

30

BNSDCCID: <WO 9744841A1\_>

This example shows the effect of various organicsoluble dispersants on the viscosity of the electrolyte-electrode mixture of Example 2.

Various commercially available dispersants were added to the mixture of Example 2, and the viscosity determined as in Example 1. The results are summarized in Table I.

10

15

Table I

Dispersant	Dosage (g/10 g SPE = 20.17 g LiMn2O4)	Viscosity (CD)	Shear Rate (sec-1)
Hypermer® KD1 (ICI)	0.2	6,200	3.4
Hypermer® KD3 (ICI)	0.2	20,200	3.4
OLOA 1200 Chevron	0.2	21,800	3.4
Hypermer® KD2 (ICI)	0.2	57,200	0.85

These results show that only the Hypermer® KDl produced a significant viscosity reduction, whereas the other dispersants actually increased viscosity.

## Example 4

This example shows the effect of the addition of acetylene black to the SPE mixture, such as would be added to form an electrolyte-electrode composite according to the present invention.

Acetylene black (Chevron)(1.36 parts) was added to 20 parts of SPE from Example 1. The rheology of this mix was determined at 125°C using a number 29 spindle. The results are summarized in Table II below.

Table II

Shear Rate (sec=1)	Viscosity (cp)
1.7	180,000
0.85	276,000
0.34	468,000
0.17	772,000

This example shows the effect of Hypermer® KD1 on the viscosity of the mixture of Example 4.

Hypermer® KD1 (0.2 parts) was added to the mixture of Example 4, and viscosity measured at 125°C with a number 29 spindle. The results are summarized in Table III below.

1.0

10

15

Table III

Shear Rate (sec <sup>-1</sup> )	Viscosity (cp)	% Reduction
1.7	32,600	82
0.85	51,000	82
0.34	115,000	75
0.17	240,000	69

The results show a 69-82% viscosity reduction with Hypermer® KD1.

## Example 6

This example shows the effect of LiMn,O, addition on the viscosity of SPE and acetylene black.

To the mixture described in Example 4 (33.6 parts SPE, 1.9 parts acetylene black) was added 25.5 parts LiMn,O. The viscosity was determined at 125°C with a number 29 spindle and is summarized in Table IV below.

Table IV

Shear Rate (sec-1)	Viscosity (cp)
1.7	142,000
0.85	233,000
0.34	370,000
0.17	750,000

This example shows the effect of Hypermer® KDl on the mixture of Example  $6. \,$ 

To the mixture of Example 6 was added 0.67 parts of Hypermer® KD1. The viscosity was determined as in Example 6. The results are summarized in Table V below.

Table V

Shear Rate (sec-1)	Viscosity (cp)	% Reduction
1.7	24,400	83
0.85	24,400	89
0.34	64,000	83
0.17	134,000	. 83

These results show that Hypermer® KD1 reduces the viscosity of a cathode mixture 82-90%.

This example shows the effect of Hypermer® KD1 on the viscosity reduction of the anode formulations. Table VI lists the formulations of each anode sample which were tested, the sample mixing conditions using the Haake Torque Rheometer, the sample viscosity measured at four different shear rates using the Instron capillary rheometer, and the sample viscosity drop due to the addition of the Hypermer® KD1 at 2200 l/sec shear rate.

- a) As shown in Table VI, Row 1 and 2, adding 1.5w% of Hypermer@ KD1 to an anode mixture having 45 v% solid loading results in a 46% viscosity reduction.
- b) As shown in Table VI, Row 1 and 3, adding 2.0 w% of Hypermer® KDI to an anode mixture having 45 v% solid loading results in a 62% viscosity reduction.
- c) As shown in Table VI, Row 4 and 5, adding 1.66 w% of Hypermer@ KD1 to an anode mixture having 50 v% solid loading results in a 9% viscosity reduction.
- d) As shown in Table VI, Row 4 and 6, adding 2.6 w% of Hypermer® KD1 to an anode mixture having 50 v% solid loading results in a 48% viscosity reduction.

5

10

15

20

TABLE VI

The effect of Hypermer® KD1 on the anode viscosity drop.

NODE HAAKE/INSTRON DATA

					ANODE	HAAKE/	ANODE HAAKE/INSTRON DATA	N DATA		i			
		FOR	FORMULATION		XIN	HIXING CONDITION	¥0.	nt 125'	Instron visc. (poise) at 125°C at sheer rate (1/sec)	poise) at ate (1/sec)			
Line No.												% visc drep at	
	O#	polid	wt 8 SP B	Hen Hypermer KD1	temp (PC)	rpm	time (min)	£	212	2269	822		
	vol.	vel											_
111	45.0	58.0	42.0	٥	115	110	13	2100	1060	534	245	٥	
(2)	45.0	58.0	43.5	1.5	115	110	οτ	1365	808	290	717	46	_
(3)	45.0	58.0	40.0	2.0	315	110	70	1245	490	204	103	62	_
(4)	20	63.0	37.0	٥	11.5	110	15	3260	1500	260	00\$		_
(5)	80	63.0	35.34	1.66	115	110	12	3840	1560	630	365	6	
(9)	80	63.0	34.4	2.60	115	110	20	1600	989	396	250	87	_

This example shows the effect of Hypermer® KD1 on the viscosity reduction of the cathode formulations. Table III lists the formulations of each cathode sample being tested, the sample mixing conditions using the Haake Torque Rheometer, the sample viscosity measured at four different shear rates using the Instron capillary rheometer, and the sample viscosity drop due to the addition of the Hypermer® KD1 at 2200 l/sec shear rate.

- a) As shown in Table VII, Rows 1 and 2, adding 2.0 w% of Hypermer® KD1 to a cathode mixture having 45 v% solid loading results in a 12% viscosity reduction.
- b) As shown in Table VII, Rows 3 and 4, adding 3.0 w% of Hypermer® KDI to a cathode mixture having 48 v% solid loading results in a 50% viscosity reduction.
- c) As shown in Table VII, Rows 5 and 6, adding 3.0 w% of Hypermer® KDl to a cathode mixture having 50 v% solid loading results in a 59% viscosity reduction.
- d) As shown in Table VII, Rows 5 and 7, adding 4.0 w% of Hypermer® KDI to a cathode mixture having 50 v% solid loading results in a 61% viscosity reduction.

20

5

10

The effect of Hypermer® KDI on the cathode viscosity drop.

ANODE HAAKE/INSTRON DATA

Instruction viac. (polse) at 125°C at shear rate (1/sec)	% visc drop at 2200 11/sec)	Ene 8130 730 730		12 3320 1320 620 300 0	12 2200 1216 545 246 12	12 5000 2170 1150 470 0	10 2560 1150 570 300 50	30 6000 2850 1600 650 0	20 3270 1150 656 310 59	9001
skron visc. (poise) at				_	Н	Н	4	-		1200
Ins 125°		520		3320	2200	2000	2560	0009	3270	2580
NOI		time (min)		12	12	13	10	30	20	30
HIXING CONDITION		Ē		110	110	110	110	20	110	110
¥		(Oa)		120	120	120	120	120	120	130
		Wt% Hypermer XD1		٥	2.0	۰	3.0	۰	3.0	
FORMULATION		vetspe		28.0	27.0	27.0	24.0	25.0	22.0	0 10
PON		pila	124	71.0	71.0	73.0	73.0	75.0	75.0	
		. G S	100	45.0	45.0	48.0	48.0	20	20	:
	Line No.			(1)	(2)	(\$)	(4)	(2)	(9)	

S

10

15

20

25

#### Example 10

This example shows the effect of Hypermer® KD1 on the anode film processability and film quality. Table VIII lists the formulations used in the extrusion/calendering process and the processing results in terms of film thickness (Film H), film width (Film W), and die flow uniformity and film dimensional stability. Table IX gives the corresponding extrusion/calendering conditions used for each of the runs.

- a) As shown in Table VIII, row 1 and 2 adding 0.5% Hypermer® KD1 to an anode mixture having 45 v% solid loading reduced the blank thickness from 15-20 mil to 10 mil, and improved the die flow uniformity, and the film width dimensional stability.
- b) As shown in Table VIII, row 3 and 4, adding 1.66% Hypermer® KD1 to an anode mixture having 50 v% solid loading greatly improve the processability. Without Hypermer® KD1 this material was not extrudable due to a very high viscosity caused by the high solid loading. Adding 1.66% Hypermer® KD1 achieved a film having 4-5 mil thick and 7-8 inches wide.

TABLE VIII - Effect of Hypermer® KD1 on the Anode Film Processing

		_				_	_
FUNDSDATES			Film Dimension Stability	Film width waried.	Film width was fairly stable at 4 inches.		Film width varied.
FUNDSDATES		เทร	word aid	Full die flow, but uneven edge tearing due to a slow flow xate.	Full die flow, fairly even and stable.	Extruder jammed.	Pull die flow, uneven, edge slow.
FOUNDMENT   FOUN		RESUI	Film W Inch	Varied		•	varied
FOUNDATION   Properset VI   Stank H   HI			Blank W Inch	7-8	•	-	7-8
FORMULATION   Paperinete Wh   B   Solid Londing   B   So	-		Film K Hil	1-5	¢-5		4-5
8011d Loading 45 Vt (58 Wt) 45 Vt (58 Wt) 50 Vt (61 Wt) 90 Vt (61 Wt)			Blank H Hil	15-20	10	-	25-30
801id Load 45 VI (58 45 VI (58 50 VI (63 50 VI (63		riow	Mypermer® We	0	6.5	0	1.66
(2) (2) (3) (4)		FORMULA	Solid Loading	45 VE (58 BN)	45 VA (58 WL)	50 VE (63 ME)	50 VE (63 HB)
		Line No.		'n.	(2)	(3)	(9)

TABLE IX - Anode Extrusion and Calendering Conditions

				-	-				j		-
	FORMULATION	Temp(1-5) (°C)	Screw (RPH)	Feed (#/hr)	88	Pressure	Tenp (*C)	Gap (mil)	Roll T(°F) top/bot	Nip gap (mil)	Roll V (ft/min)
(1)	45.0 vt (Saut) Of Hypermeré KOl	115-115-115-110-78	130	17-25	14	091	121		097/54	1-1.5	9-18
(2)	45.0 vt (584t) 0.5t Hypermere XD1	123-123-120-95-75	130	17-25	01	025-059	128	1.5-2	097/59	1-1.5	2
(3)	50 vt (63vt) Ot Hypermere KD1	120-120-120-95-75	311	17-28	12	12 >2400 Extruder Jammed	125	e	072/54	1-2.5	1-15
(3)	50 vt (63wt) 1.664 Mypermer® KD1	121-121-121-95-75	130	17-25	п	810	126	1	45/240	1-1.5	8-15
	7.5	The state of the s									

The corresponding processing results are given in Table VIII, under the same line number

b)

#### Example 11

This example shows the effect of Hypermer® KD1 on the cathode film processability and film quality. Table X lists the formulations used in the extrusion/ calendering process and the film processing results in terms of film thickness (Film H), film width (Film W), as well as die flow uniformity and film dimensional stability. Table XI gives the corresponding extrusion/calendering conditions used in each of the runs.

- a) As shown in Table XI, row 1 and 2, adding 2% Hypermer® KD1 to a cathode mixture having 45 v% solid loading improved the die flow uniformity thus improved the film width stability.
- As shown in Table XI, row 3 and 4, adding 3.0% Hypermer® KD1 to a cathode mixture having 48 v% solid loading greatly improve the processability. Without Hypermer® KD1 the die flow was very uneven, and large portion of the die was blocked due to high viscosity of the material. Adding 3% Hypermer® KD1 greatly reduced the die blocking, improved the die flow uniformity, and stabilized the process. We were able to get a film with 7 inch wide and the process was fairly stable and lasted for 20 minutes.

20

5

10

15

TABLE X Effect of Hypermer® KD1 on Cathode Film Processing

		_	_		
	Film Dimension Stability	Film width varied considerably.	Die flow was fahrly Pilm width was fahrly stable at edge blocked.	Film width varied considerably.	Film width was fairly stable at 7.5 inches. The process continued for 20 minutes.
.75	Die Flow	Die blocked sarlously, Uneven tlow, strips,	Die flow was falrly even and stable. Die edge blocked.	Die blocked meriously. Severe, uneven flow.	Die flow was fairly even and stable.
RESULTS	Film W Inch	varied	6.5	varied	7.5
	Blank W Inch	4.5	9	£-3	4
	Film H Kil	1-1	6-9	4-1	9-10
	Blank H Mil	12-15	10-12	15-16	13-15
TICK	Hypermare Wt	o	2	٥	•
FORKULATION	Solid Loading	45.4 Vh (72 Nh)	45.4 VN (71 NV)	48 V\$ (73 H\$)	(40 (12 14)
Line No.		(1)	(2)	(6)	93

TABLE XI Cathode Extrusion and Calendering Condition

_	FIRE NO.		EXTRUDER	25				Id	DIE		CALENDER	
		FORMULATION	Temp(1-5) (°C)	Screw (RPH)	faed (#/hr)	88	Pressure (psi)	Tenp (°C)	Gap (m.11)	Roll T("F) top/bot	Wip gap (Lin)	Roll V (ft/min)
	111	45.4 of (71wt) of Hyperhere KDl	118-118-110-95-75	130	45-60	49-56	450-550	128	3	45/240	Z-T	11
	(2)	45.4 vt (71vt) 21 Hypermer® KD1	120-120-120-95-75	:30	37	10	380-400	115	2-3	45/240	1-1	8-10
	(8)	48 v\$ (73w%) O' Hypermer® XD1	134-127-124-117-134	160	60-50	46	46 2100-900	130-135		457240	1-2	
	(93	48 vt (73wt) 34 Hypermer® XD1	118-218-110-95-75	150	38-60	15	15 670-690	120	3	45/240	1-2	11-13
P.								,				

the same line number. The corresponding processing results are given in Table X under

3NSDCCID: <WO\_\_\_\_\_9744841A1\_i\_>

This example shows that Hypermer® KD1 does not adversely affect cell performance. Cells were prepared with and without Hypermer® KD1. The data in the following Table XII are the average performances of three control cells and three Hypermer® KD1 cells, respectively. Both cells were made with 5 mm coke (Conoco). At cycle 30, the Hypermer® KD1 cells have an average capacity of 6.3 mAh, with a current efficiency of 100% (within the error of the measurement). There has been no measurable degradation since cycle 5.

15

20

10

5

Table XII

Cell	Theoretical Capacity (LiC)	Capacity (LiMn O,) (100mAh/g)	Capacity Cycle 1	Efficiency Cycle 1	Capacity Cycle 5	Efficiency Cycle 5
Control	22 mAh	11.3 Mah	6.2 mAh	54.6%	7.8 mAh	96.8%
Control + 2% Hypermer® KD1	13.7	12,1	4.7	54.3	6.3	98.7

Although the present invention has been described in relation to particular embodiments thereof, many other variations and modifications and other uses will become apparent to those skilled in the art. The present invention is to be limited not by the specific disclosure herein, but only by the appended claims.

10

15

20

25

30

#### What is Claimed is:

- An electrode composition containing an electrically active powder in a solid polymer and, as a dispersant, a polyester polyamine copolymer that is electrochemically inert.
- 2. A composition according to claim 1 wherein said electrode is a cathode and said electrically active powder is lithium manganese dioxide (LiMn,0,) or overlithiated manganese oxide.
- 3. A composition according to claim 2 wherein said composition comprises ethylene carbonate, propylene carbonate, polyacrylonitrile, lithium (bis)trifluoromethanesulfonimide, LiMn,O<sub>4</sub>, acetylene black, and said dispersant.
- 4. A composition according to claim 1 wherein said electrode is an anode and said electrically active powder is carbon capable of having lithium ion intercalated within its structure.
- The composition according to claim 1 wherein said dispersant is electrochemically inert at 2.5-4.5 volts.
- The composition according to claim 1 wherein said dispersant is electrochemically inert at 2.5-4.2 volts.

# INTERNATIONAL SEARCH REPORT

CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01M 4/62

International application No. PCT/US97/08032

US CL According	:429/ 214, 215, 217, 218, 250 to International Patent Classification (IPC) or to b	oth national classification and IPC	
	LDS SEARCHED		
Minimum	documentation scarched (classification system follo	wed by classification symbols)	
U.S. :	429/ 214, 215, 217, 218, 250		
Documents	ation scarched other than minimum documentation to	the extent that such documents are include	d in the fields searched
	data base consulted during the international search see Extra Sheet,	(name of data base and, where practicable	t, search terms used)
C. DOC	CUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where	appropriate, of the relevant passages	Relevant to claim No.
×	US 5,358,801 A (BRODD) 25 O 9-21; col. 6, lines 26-60; col. 15	ctober 1994, col. 14, lines 5, lines 31-35.	1
A	US 3,918,989 A (GILLMAN et al	l.) 11 November 1975	1-6
A	KIM, YOUNG-WOOK et al., Tape Materials Research Society Fa November 1992. (Abstract)	Casting of Silicon Nitride, Il Meeting, Boston, MA,	1-6
	-		
Furthe	er documents are listed in the continuation of Box (	C. See patent family annex.	
	cial categories of cited documents; ament defining the general state of the art which is not considered o of particular relevance	"I" inter document published after the inter- date and not in conflict with the applicate principle or theory underlying the inver-	national filing date or priority ion but cited to understand the
E* certification of the control of the certification of the certificatio	ier document published on or after the intermelienal filling date mustar which may furew doubte on priority chain(s) or which is to contablish the publication date of another chaines or other isl reason (as specified) and other chains or other one of the contable of the contable of the contable or other to	"X" decuncat of periodar relevance; the considered sovel or cannot be considered when the decument is taken alone."  "Y" decument of particular relevance; the considered to involve an invente considered to involve an invente combined with one or more other make being obvious to a person aktilité or person aktilité o	claimed invention cannot be d to involve an inventive step claimed invention cannot be step when the document is document and combination
docu the p	ment published prior to the international filing date but later than priority date claimed	"A" document member of the same patent for	really contract of the contrac
ate of the a	ctual completion of the international search	Date of mailing of the international sear 2 6 SEP 1997	ch report
ame and ma	ailing address of the ISA/US	Authorized officer	<del>/ / `</del>

Box PCT washington, D.C. 20231
Facsimile No. (703) 305-3230
Form PCT/ISA/210 (second sheet)(July 1992)\*

# INTERNATIONAL SEARCH REPORT

International application No. PCT/US97/08032

CA, WPIDS, INSPEC, COMPENDEX, USPATFULL carch terms: Hypermer?; polyester# or polyamine#; electrode# or cathode# or anode#; electrochem? (3a) (finert or nonconduct? or conduct?)			
	÷		

Form PCT/ISA/210 (extra sheet)(July 1992)\*